



In-situ synthesis of Ni₂P co-catalyst decorated Zn_{0.5}Cd_{0.5}S nanorods for high-quantum-yield photocatalytic hydrogen production under visible light irradiation

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ABSTRACT

Efficient noble-metal-free semiconductor composite photocatalysts are highly desirable for visible light driven water splitting. In this study, Ni₂P was successfully decorated on Zn_{0.5}Cd_{0.5}S as a highly efficient co-catalyst via a hydrothermal method. The chemical as well as photophysical properties of the as-obtained Ni₂P/Zn_{0.5}Cd_{0.5}S samples were characterized by X-ray diffractometry (XRD), Transmission electron microscope (TEM), UV–vis diffusion reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and time-resolved fluorescence. The Ni₂P/Zn_{0.5}Cd_{0.5}S composite sample with 4% molar content of Ni₂P showed the highest photocatalytic H₂ evolution activity with a corresponding H₂ evolution rate of 1173 μmol h^{−1}, which was about 13 times higher than that of pure Zn_{0.5}Cd_{0.5}S sample under visible light irradiation. The photocatalytic activity of the Ni₂P/Zn_{0.5}Cd_{0.5}S composite sample was stable even after 4 cycling photocatalytic experiments. A possible mechanism on the photocatalytic enhancement of the Ni₂P/Zn_{0.5}Cd_{0.5}S composite sample was systematically investigated, which can provide a novel concept for the synthesis of other desirable semiconductor materials with high photocatalytic performance.

1. Introduction

The great advance in the development of human society achieved in last century has also caused tremendous energetic and environmental problems. Benefiting from the Honda-Fujishima effect discovered in 1972 [1], solar driven photocatalytic hydrogen production via water splitting was realized and has been studied extensively as a promising solution to address those issues [2–6]. Various semiconductors such as oxides [7–9], metal sulfides [10–12], and oxynitrides [13,14] have been investigated as potential candidates for efficient photocatalytic H₂ evolution through water splitting. However, none of them meet the needs for practical application, and visible light responsive photocatalyst with excellent charge separation ability and high solution stability still remains as a huge challenge.

Among the various semiconductor photocatalysts which were developed in last decades for photocatalytic H₂ evolution, Zinc cadmium sulfide (Zn_{0.5}Cd_{0.5}S) has received considerable attention due to its appropriate bandgap and high photocatalytic activity [15–17]. In

addition, Zn_{0.5}Cd_{0.5}S also exhibits many excellent properties for practical application, including high stability, simple to synthesize and elemental abundant in natural reserves [18,19]. However, its intrinsic drawbacks, in particular low specific surface area, fast charge recombination and narrow light absorption range, have inhibited the further development of Zn_{0.5}Cd_{0.5}S and should be well addressed. The catalytic activities of Zn_{0.5}Cd_{0.5}S are determined the morphology and the micro crystal structure [20]. To enhance the photocatalytic activity of Zn_{0.5}Cd_{0.5}S, loading suitable co-catalysts to capture photo-induced charges and provide rich active sites for surface redox reaction has been demonstrated to be a useful approach. To date, various co-catalysts have been employed to combine with sulfides, including noble metals [21–23], transition metal oxides [24–26], transition metal sulfides [27–29], and hydroxides [30].

However, the most effective major co-catalysts today are predominantly relied on high-cost precious metals which are not suitable for large scale applications [31,32]. Therefore, it is an urgent task to explore the catalytic ability of low-cost non-noble metal co-catalysts for

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photocatalytic hydrogen evolution. Recently, transition-metal phosphides have been studied as co-catalysts, and several groups have shown that transition-metal phosphides, such as Co_2P [33], Cu_3P [34,35], CoP [36,37] and FeP [38,39], can be used as co-catalyst to effectively enhance the catalytic performance of photocatalysts. Compare to other noble-metal-free co-catalysts mentioned above, nickel phosphide exhibit many attractive advantages, including high activity of hydrogen production, long term stability [40,41], etc. Therefore nickel phosphides are considered as one of the best alternatives of noble metal co-catalysts.

Motivated by the transition-metal phosphides co-catalysts research mentioned above, herein we prepared one-dimensional $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalysts via hydrothermal synthesis method. Detailed characterizations on the morphology, crystal structure, chemical states, and optical properties of the composite photocatalysts were carried out. The photocatalytic H_2 evolution activity and stability of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ under visible light irradiation was also characterized. The apparent quantum yield of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ for hydrogen production can reach as high as 18.1% at 420 nm. The possible photocatalytic mechanism for enhanced H_2 evolution activity was proposed. Our experimental results demonstrated that Ni_2P can act as an effective co-catalyst for $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ which indicates that it may be also potentially benefiting for other semiconductor photocatalysts for H_2 evolution.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}$, Aladdin), cadmium acetate dihydrate ($\text{Cd}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}$, Aladdin), thioacetamide (A.R), red phosphorus (A.R), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$, A.R), ethyl alcohol (EtOH, A.R.), ethylenediamine (A.R), sodium sulfide (A.R), and sodium thiosulfate (A.R) were used as received without additional purification or treatment. Deionized water was used in all experiments.

2.2. Synthesis of the photocatalysts

The $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample was prepared according to our previous work with a slight modification [16]. A total of 10 mmol equimolar of zinc acetate dihydrate and cadmium acetate dihydrate were added into 60 ml of ethylenediamine with stirring followed by another addition of 20 mmol thioacetamide. After vigorous stirring for 1 h at room temperature, the white solution was transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 24 h. After that, the product was washed by centrifugation with distilled water and ethanol for several times, respectively. Finally, the pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample was obtained via drying the washed solution under vacuum at 60 °C overnight.

The $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites were prepared by hydrothermal method. First, 0.4 g of as-prepared $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample was dispersed in 60 ml of deionized water under stirring, and then a calculated amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and red phosphorus (the molar ratio of Ni to P is 1:5) were added. The mixture was sonicated for 3 h, then the mixed solution was transferred into a 100 ml Teflon-lined autoclave and heated at 200 °C for 24 h. After that, the products were washed by centrifugation with deionized water and ethanol for three times, respectively. And the final product was obtained by drying the washed solution under vacuum at 60 °C overnight. The molar percentages of Ni_2P in the prepared composite catalyst were 0%, 0.5%, 1%, 2%, 2.5%, 3%, 4% and 5%, respectively.

2.3. Characterization

The X-ray diffractometer (XRD) using $\text{Cu K}\alpha$ as radiation was applied to investigate the crystallographic texture of all samples with 2 θ range from 20° to 65°. The morphology of all samples was identified by

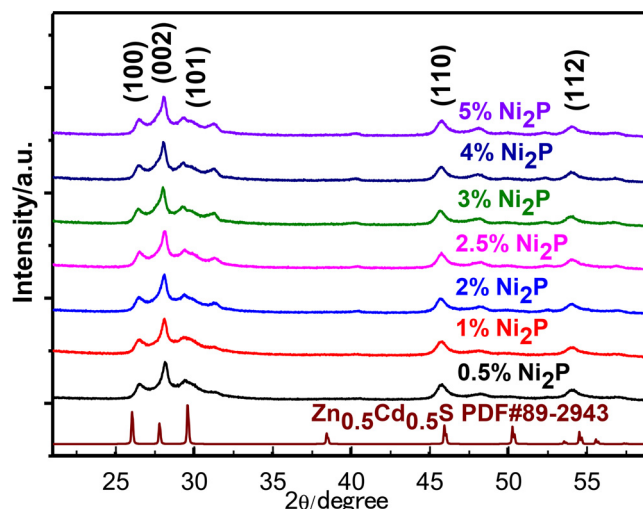


Fig. 1. XRD patterns of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites with different weight ratios of Ni_2P .

transmission electron microscopy (TEM, JEM-2100, accelerating voltage 200 kV). The UV–vis diffuse reflection spectroscopy (DRS) of all samples was detected by Shimadzu UV-4100 spectrophotometer, and the reflection from BaSO_4 powder was used as a reflectance standard. X-ray photoelectron spectroscopy (XPS, PHI 5300 ESCA system) was applied to analyze the element valence state of the composite sample, the signal of carbon at 284.8 eV was used as a reference to calibrate the binding energies. The PL spectra of the photocatalysts were detected using a Varian Cary Eclipse spectrometer with an excitation wavelength of 340 nm.

2.4. Photocatalytic activity

The photocatalytic H_2 evolution was carried out in a 300 ml quartz reactor (Perfectlight Labsolar IIAG system), which was connected with a low-temperature thermostat bath to keep the reaction temperature at 4 °C during the characterization. The light source (PLS-SXE 300UV Xe arc lamp) was 1 dm over the reactor to illuminate the reactants with light intensity of 11.0 mW/cm^2 . In a typical photocatalytic H_2 evolution experiment, 50 mg of photocatalyst was dispersed in 100 ml of mixed aqueous solution with constant stirring, in which the mixed aqueous solution is composed by 100 ml water and 0.35 M Na_2S and 0.25 M Na_2SO_3 as sacrificial reagents. Before each photocatalytic H_2 evolution experiment, the reaction system was evacuated for 30 min to create an anaerobic condition. A gas chromatography (Beifen 3420 A, TCD) was selected to analyze the products, and high purity Argon was utilized as carrier gas.

The apparent quantum yield (ϕ) for H_2 evolution was determined for the photocatalytic system containing 50 mg 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, 0.25 M Na_2S and 0.35 M Na_2SO_3 in 100 ml deionized water. The solution was irradiated by 420 nm (± 5 nm) visible light irradiation. The apparent quantum efficiency (AQE) could be calculated according to Eq. (1).

$$\text{AQY}(\%) = \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100 \quad (1)$$

2.5. Density functional theory (DFT) calculation

All calculations were performed using DFT within the plane-wave pseudopotential as implemented in the VASP code with a cutoff energy of 350 eV. The Perdew, Burke, and Ernzerhof (PBE) [42] exchange-correlation functional within a generalized gradient approximation (GGA) was employed. The PAW method was used to describe the effect

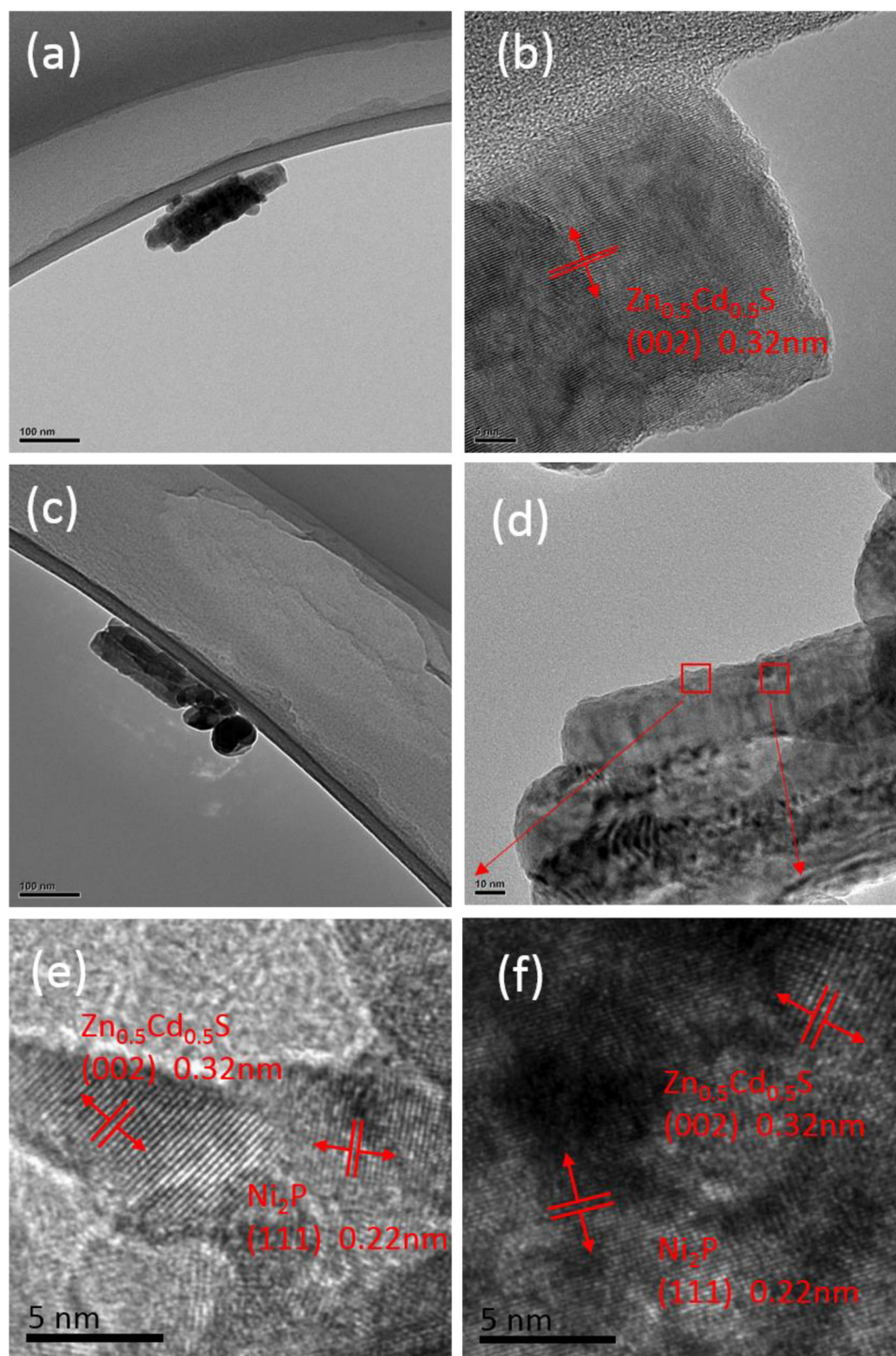


Fig. 2. TEM images of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample (a), $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite (c, d); HRTEM image of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample (b), $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite (e, f).

of core electrons [43,44]. Gamma-centered k-point meshes of $2 \times 2 \times 1$ were used. The atomic positions were relaxed until the force on each atom was less than $0.05 \text{ eV}/\text{\AA}$. Using the periodic slab model and self-consistent dipole correction, the averaging electrostatic potential in the planes perpendicular to the slab normal could be obtained.

Bulk $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ forms a tetragonal lattice with space group P63mc and experimental lattice constants are: $a = b = 3.95 \text{ \AA}$, $c = 6.42 \text{ \AA}$. Bulk Ni_2P forms a tetragonal lattice with space group P-62m and experimental lattice constants are: $a = b = 5.86 \text{ \AA}$, $c = 3.38 \text{ \AA}$. We built a periodic slab with four and four layers for $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (002) and Ni_2P (111) facets, respectively. 2×2 and 1×1 surface unit cells were used,

respectively. The bottom two layers of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and Ni_2P are fixed, while the top two layers are relaxed during the calculation. The vacuum gap thickness was set to be 12 \AA . The heterostructures are modelled by an interface with 20 \AA vacuum to avoid interactions between the adjacent slabs.

3. Results and discussion

3.1. Characterization of $\text{Ni}_2\text{P}/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ composite samples

The phase purity and crystal structure of the as-prepared samples

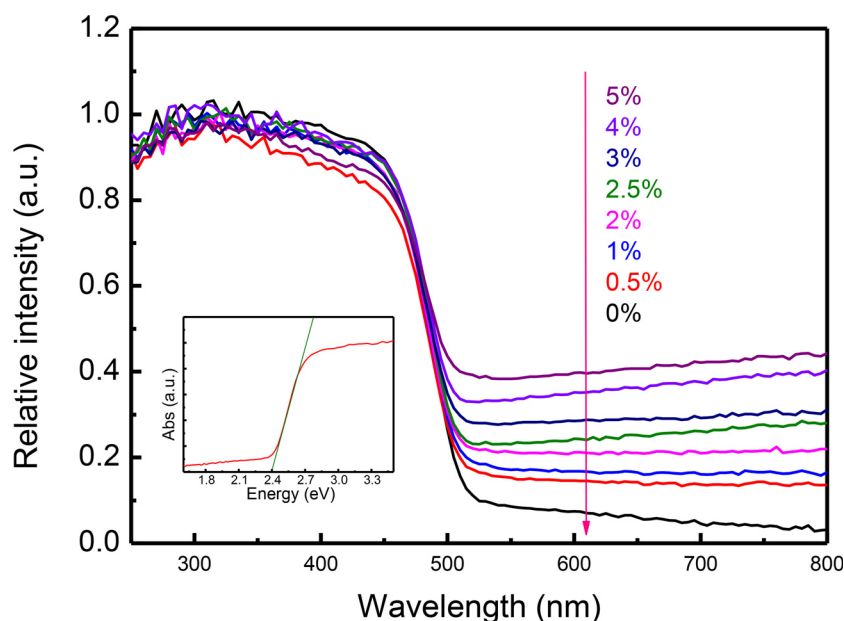


Fig. 3. UV-vis diffuse reflectance spectra of pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites with different molar ratios of Ni_2P .

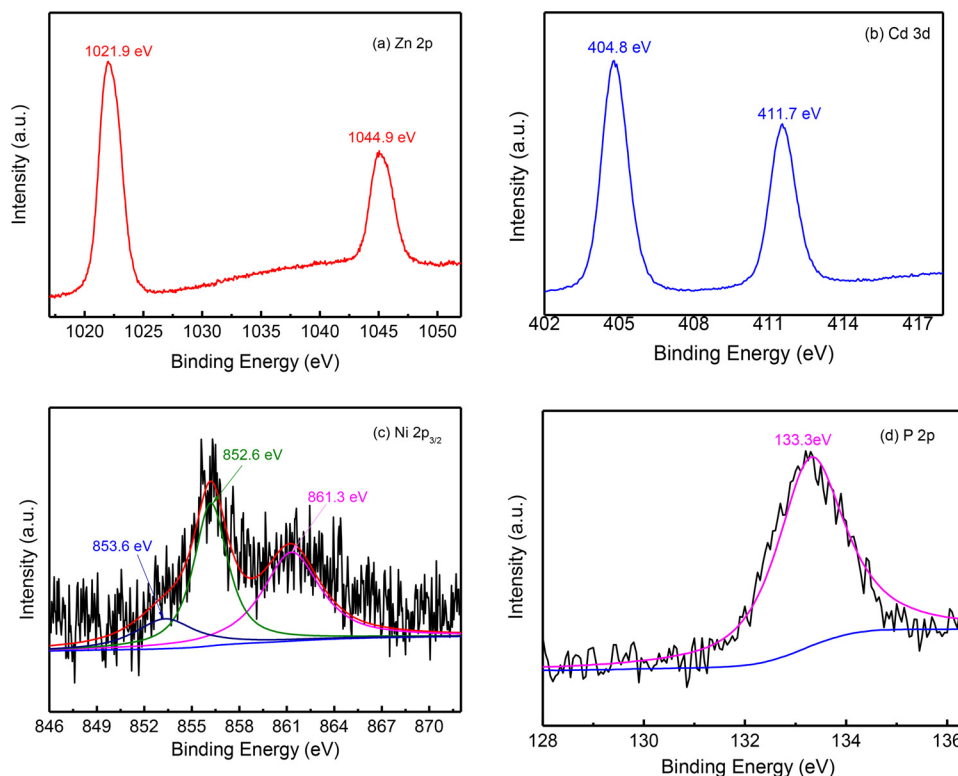


Fig. 4. XPS spectra of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples: (a) Zn 2P; (b) Cd 2d; (c) Ni 2p; (d) P 2p.

were determined by XRD analysis. Representative XRD patterns of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ are shown in Fig. 1, and the data of the standard card of hexagonal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (JCPDS No. 89-2943) is also shown as reference. The main peaks of 2θ at 26.11° , 27.76° , 29.62° , 46.02° and 54.58° can be readily indexed to the (100), (002), (101), (110) and (112) planes of hexagonal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, respectively. It is obvious that the deposition of Ni_2P did not affect the crystal structure of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. However, no apparent diffraction peak of Ni_2P was observed in all composite samples, which may indicate that the deposition content of Ni_2P in all the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite samples is quite low which exceeds the sensitive of XRD characterization. Nevertheless, the

presence of Ni_2P in the composites can be easily proved by TEM and XPS techniques as will be discussed later.

To gain insight into the microstructure details of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, the morphology of the as-prepared samples was characterized by TEM and HRTEM. As shown in Fig. 2 (a), it can be seen that pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample has a rod-like morphology with an average diameter of ~ 40 nm and length of $100\text{ nm} \sim 200\text{ nm}$. The morphology of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ after the chemical reduction deposition of Ni_2P is shown in Fig. 2(c), reveals that Ni_2P was deposited as nanoparticles on the surface of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ with high dispersion, and no other obvious changes in the microstructure of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanorods can be found. Fig. 2(b) and Fig. 2(d–f) present the

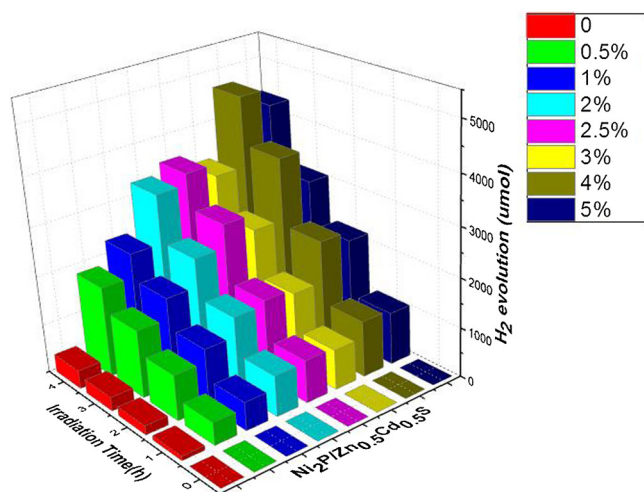


Fig. 5. Photocatalytic H_2 evolution over $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite samples with different Ni_2P contents under visible light.

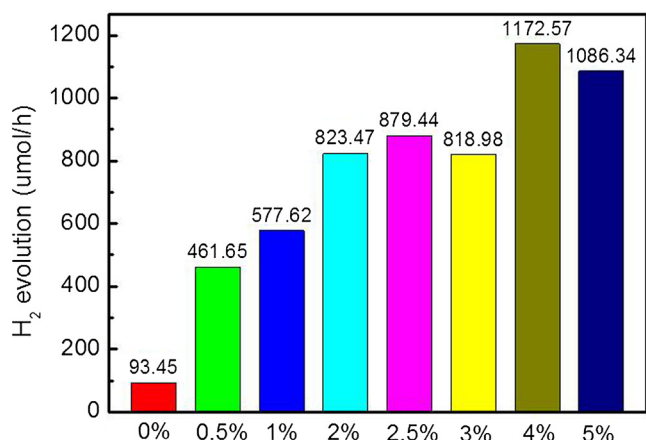


Fig. 6. Rate of H_2 evolution over $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite samples with different Ni_2P contents.

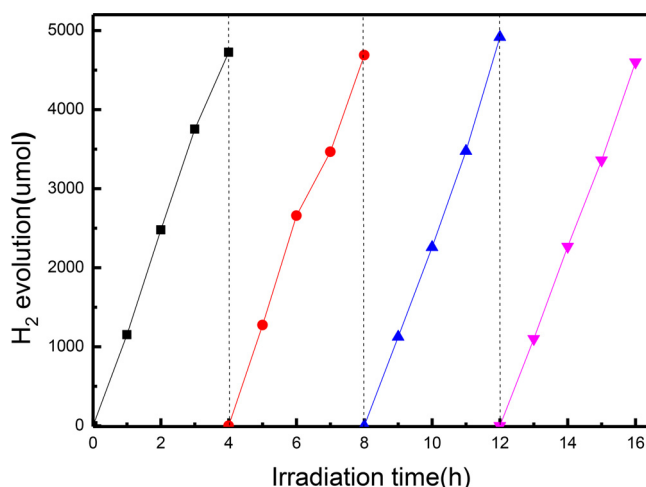


Fig. 7. Cycling runs for the photocatalytic H_2 evolution in the presence of the 4% $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite sample under visible light irradiation.

HRTEM images of the $Zn_{0.5}Cd_{0.5}S$ and $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite samples, different orientation and interplanar spacing were observed. The identified lattice fringe spacing of 0.32 nm corresponds to the (002) lattice plane of $Zn_{0.5}Cd_{0.5}S$. With the deposition of Ni_2P , a new

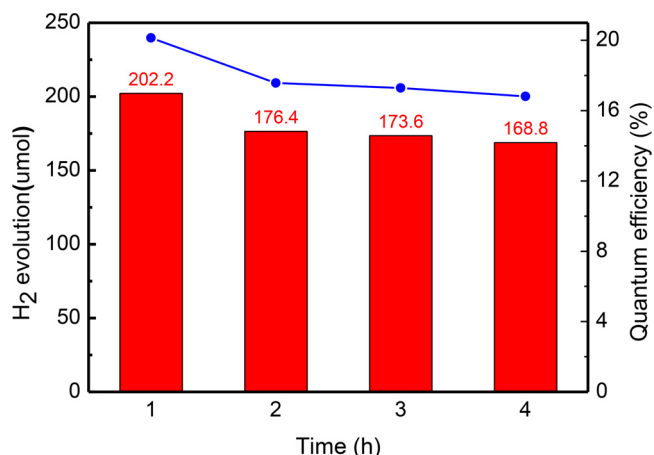


Fig. 8. The photocatalytic H_2 evolution and quantum efficiency in the presence of the 4% $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite sample under 420 nm light irradiation.

interplanar spacing of 0.22 nm can be seen, which can be ascribed to the (111) lattice plane of Ni_2P [45]. The TEM and HRTEM characterization results indicate that an intimate contact interface is formed between Ni_2P and $Zn_{0.5}Cd_{0.5}S$ components in the $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite sample, which could serve as a critical role for effective improvement of the separation efficiency of photo-generated electrons-hole pairs.

The UV–vis diffuse reflectance spectra (DRS) of the as-prepared $Zn_{0.5}Cd_{0.5}S$ and $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite samples were performed to characterize their light-absorbing abilities. As shown in Fig. 3, the pure $Zn_{0.5}Cd_{0.5}S$ sample shows absorption from UV to the visible range with an abrupt decline at ~ 500 nm, which gives an information to its optical band gap. The band gap of $Zn_{0.5}Cd_{0.5}S$ is determined to be about 2.4 eV by Tauc's plot as shown in the Fig. 3 insert, which is consistent with the value reported previously [46]. After deposition of Ni_2P co-catalyst, all of the $Ni_2P/Zn_{0.5}Cd_{0.5}S$ samples have a similar abrupt decline in light absorption at ~ 500 nm, but exhibit a remarkable enhanced light absorption in the visible region compared with pure $Zn_{0.5}Cd_{0.5}S$. The absorption intensity of the as-prepared samples in the visible range is strengthened with increasing the deposition content of Ni_2P , which agrees with the color change of the prepared samples from light yellow to hazel-green. The DRS results demonstrate that the chemical in-situ deposited Ni_2P has considerable positive influence on the utilization of visible light, and hence the $Ni_2P/Zn_{0.5}Cd_{0.5}S$ composite sample is expected to have superior photocatalytic performance.

The X-ray photoelectron spectroscopy (XPS) analysis was performed to investigate the surface chemical states of the $Ni_2P/Zn_{0.5}Cd_{0.5}S$ sample. It can be seen that the binding energy spectrum of Cd shows two peaks at 405.0 and 411.7 eV (Fig. 4a), which are corresponding to Cd 3d_{5/2} and Cd 3d_{3/2} respectively, indicating that the valence state of Cd element is +2. As shown in Fig. 4b, the binding energies of Zn 2p_{3/2} and Zn 2p_{1/2} were determined to be 1021.9 and 1044.9 eV, which confirmed the presence of Zn²⁺. This result agrees well with the values reported in our previous work [18,19]. Fig. 4c shows the XPS spectrum of Ni 2p_{3/2}. The peak at 853.3 eV was assigned to Ni²⁺ of Ni_2P , and the other two peaks at 856.2 eV and 861.3 eV correspond to surface oxidation states [45]. Meanwhile, as shown in Fig. 4d, only one peak at 133.3 eV can be found for the P 2p of Ni_2P [47,48]. Based on the XPS characterization results, we can conclude that Ni_2P is successfully deposited on the $Zn_{0.5}Cd_{0.5}S$ surface.

3.2. Photocatalytic H_2 evolution activity

The photocatalytic activities of the as-prepared samples were investigated in Na₂S and Na₂SO₃ aqueous solution under visible-light irradiation and the results are shown in Fig. 5. Control experiment of

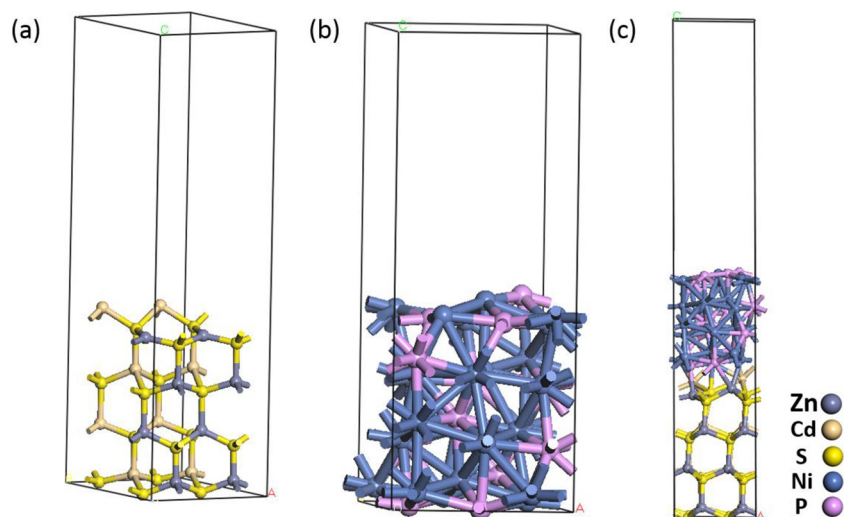


Fig. 9. The calculation model for pure samples of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (a), Ni_2P (b) and the heterojunction metal-semiconductor structure of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (c).

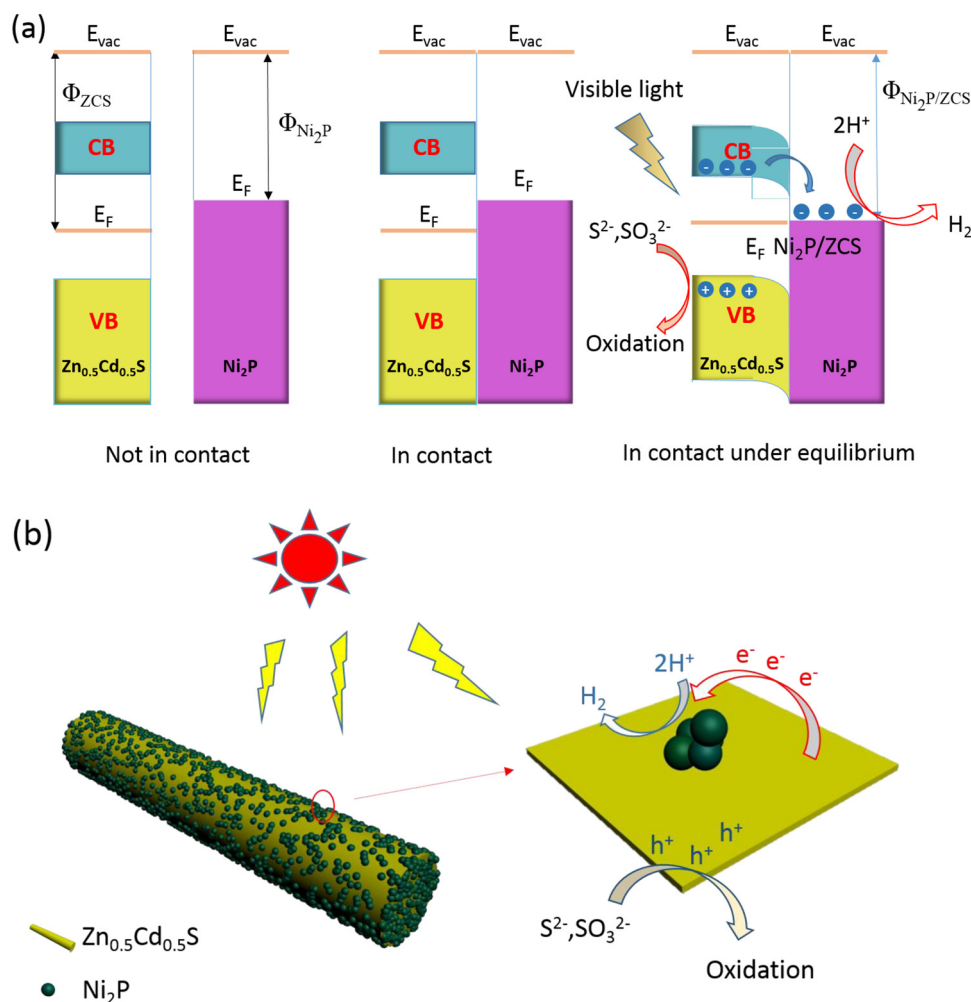


Fig. 10. Schematic illustration of charge transfer and H_2 evolution mechanism of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ under visible light irradiation.

pure Ni_2P sample for H_2 evolution evaluation is also carried out; the control experiment result shows that pure Ni_2P has no photocatalytic H_2 evolution activity. The pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample without Ni_2P deposition exhibits a low photocatalytic H_2 production activity of $93 \mu\text{mol h}^{-1}$. After introducing Ni_2P , all of the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite samples exhibit a significantly enhanced activity of

photocatalytic hydrogen production. Fig. 6 presents the photocatalytic H_2 evolution rate of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite samples with different Ni_2P deposition contents. After loading 0.5% Ni_2P on $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanorods, the H_2 evolution activity is remarkably increased to $461 \mu\text{mol h}^{-1}$. Along with increasing the deposition content of Ni_2P , the photocatalytic H_2 evolution rate is further improved. The 4% $\text{Ni}_2\text{P}/$

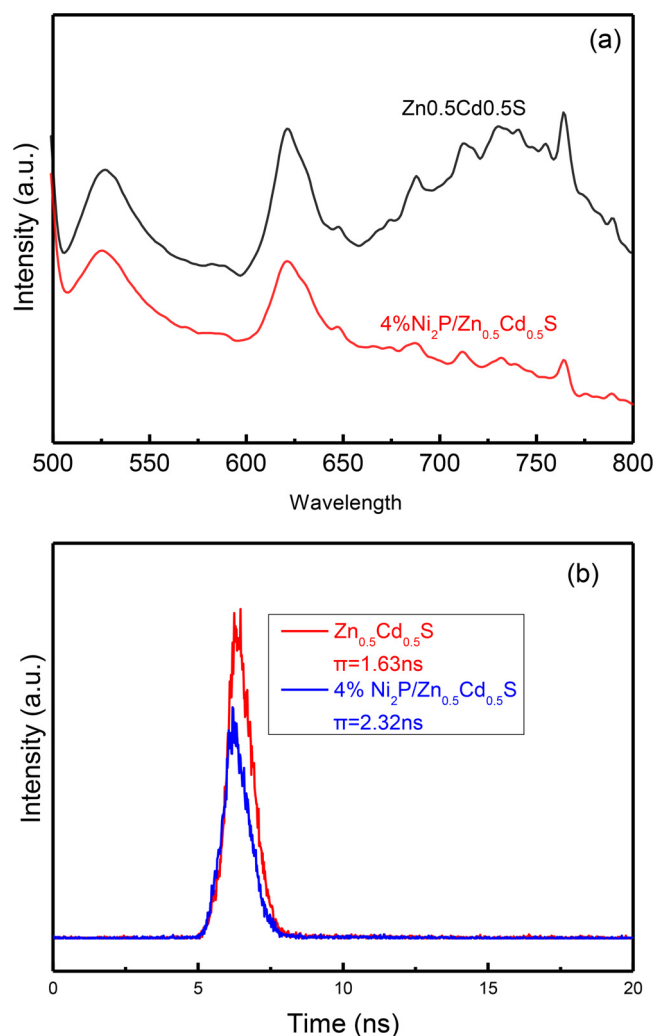


Fig. 11. (a) PL spectra of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples. (b) The time-resolved fluorescence spectra of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples.

$\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample presents the highest H_2 evolution activity with a H_2 evolution rate of $1172 \mu\text{mol h}^{-1}$, which is 13 times higher than that of pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. However, further increasing the deposition content of Ni_2P beyond 4% leads to a decrease in photocatalytic H_2 evolution rate. The decrease in the photocatalytic activity may be due to the high loading ratio of black Ni_2P , which would inhibit the light absorption of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, leading to a reduction in the number of photo generated carriers. Thus, the competition of light absorption between Ni_2P and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ should be the key parameter for the deterioration in photocatalytic H_2 evolution rate. Therefore, a suitable loading amount of Ni_2P is important for the optimization of the photocatalytic activity of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite samples.

The stability of a photocatalyst is highly critical for practical applications. To investigate the durability of the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalyst, the photocatalytic activity of the 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample was investigated via cycling test of photocatalytic H_2 evolution experiments. Fig. 7 illustrates the H_2 evolution curves in cycling photocatalytic run. The H_2 production rate does not display obvious decrease after being irradiated for 16 h (4 cycles), which indicates that the 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalyst has sufficient stability for photocatalytic H_2 production.

Moreover, in order to further evaluate the photocatalytic activity of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, its apparent quantum yield was measured at 420 nm ($\pm 5 \text{ nm}$). One molecule of H_2 is assumed to be generated by the

absorption of two photons. The result of apparent quantum yield is shown in Fig. 8. The average rate of H_2 evolution is $\sim 202 \mu\text{mol h}^{-1}$ which sets ϕ to be 18.95%. This high apparent quantum yield for photocatalytic H_2 evolution stands for an efficient conversion of visible light energy, suggesting that the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite photocatalyst is highly active for electron-hole pair generation and separation. Thus, it can be seen that $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ is an efficient photocatalyst for visible-light-driven photocatalytic H_2 evolution.

3.3. Photocatalytic mechanism investigation

It is important to clarify the underlying reason for the significant improvement in the photocatalytic H_2 evolution performance of these Ni_2P modified $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples. We then calculated the work function of the materials via preliminary density functional theory (DFT) to reveal the charge injection behaviors at the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ interface. The calculation model of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (002), Ni_2P (111) and the heterojunction metal-semiconductor structure of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (002)/ Ni_2P (111) is shown in Fig. 9(a, b, c). In this system, the work functions of the metallic Ni_2P (111) and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (002) are 4.94 eV and 6.78 eV, respectively. As is well-known, different work function of metal and semiconductor will results in energy band bending when they are bring into intimate contact [49,50]. Therefore, when $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and Ni_2P form intimate contact, the electrons will transfer from Ni_2P to $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ as the Fermi level of Ni_2P is higher than $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, and leading to a downward energy band bending at the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ interface. After the electronic equilibrium of the heterojunction system is reached, the unified work function was observed to be 6.02 eV.

Based on the calculation of work function and the photocatalytic H_2 evolution performance of $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, a possible mechanism for the enhanced photocatalytic H_2 evolution activity of the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalyst is proposed. As depicted in Fig. 10(a, b), $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ absorbs photons and generates electron-hole pairs under visible-light irradiation. However, without the deposition of Ni_2P co-catalyst, the photo-generated electrons and holes are likely to recombine rapidly which leads to a low photocatalytic H_2 production activity. After depositing Ni_2P on the surface of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, the photo-induced electron will transfer rapidly from $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ to Ni_2P due to the strong internal potential field formed at the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ interface, and then reduce H^+ to H_2 via the active sites present at the surface of Ni_2P . The photo-induced holes will be accumulated on the surface of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and are consumed by Na_2S and Na_2SO_3 sacrificial reagents [18,50]. As a consequence, the Ni_2P can act as an electron collector and transporter to prolong the lifetime of the charge carriers, thus improving the photocatalytic activity of the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples.

To verify the proposed mechanism for the enhanced photocatalytic performance in the Ni_2P composite sample, photoluminescence (PL) spectra of pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite sample were obtained to probe the status of radiative recombination of the photo-generated charge carriers. A high recombination rate of excited holes and electrons in the photocatalyst generally results in a low photocatalytic activity [4]. As shown in Fig. 11(a), it was found that the PL intensity of 4% $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ is lower than the pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. The results clearly indicate that the presence of Ni_2P is favorable for suppressing the recombination process of electron-holes, leading to high photocatalytic hydrogen production activity. Therefore, a noticeable enhancement in the photocatalytic activity is achieved in the $\text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite sample. The PL results fitted well with the energy band analysis result and photocatalytic activity characterization of the samples. To give a further evidence for the proposed photocatalytic mechanism, the dynamic behavior of photo-generated charge carriers was also investigated with the assistance of time-resolved fluorescence spectroscopy (Fig. 11(b)). It can be seen that the PL decay lifetime of the photocatalyst increases in the order of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S} < \text{Ni}_2\text{P}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, and the lifetime was determined to be 1.63 ns and 2.32 ns,

respectively. The time-resolved fluorescence result clearly confirm that the recombination of photogenerated charge carriers is indeed suppressed in the Ni₂P/Zn_{0.5}Cd_{0.5}S nanorod samples.

4. Conclusions

In summary, a highly efficient composite and noble-metal-free photocatalyst Ni₂P/Zn_{0.5}Cd_{0.5}S was prepared via hydrothermal method. The Ni₂P NPs are dispersed uniformly on the surface of Zn_{0.5}Cd_{0.5}S nanorods and form intimate contact interfaces. A highest H₂ amount as high as 1172 μmol h⁻¹ was obtained in 4% Ni₂P/Zn_{0.5}Cd_{0.5}S sample, which is 13 times than that of pure Zn_{0.5}Cd_{0.5}S. In addition, the 4% Ni₂P/Zn_{0.5}Cd_{0.5}S sample also exhibited a good stability in the cycling photocatalytic experiments. Finally, combined with the DFT calculation result of the Ni₂P/Zn_{0.5}Cd_{0.5}S heterojunction structure, a possible photocatalytic mechanism is proposed to explain the observed H₂ evolution activity enhancement in the Ni₂P decorated Zn_{0.5}Cd_{0.5}S sample, which was further confirmed by photoluminescence (PL) and time-resolved fluorescence characterizations. Therefore, our experimental results demonstrated that Ni₂P is a promising co-catalyst for Zn_{0.5}Cd_{0.5}S, which can also be regarded as potential functional co-catalyst to promote the photocatalytic H₂ production activity of other semiconductor photocatalysts.

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